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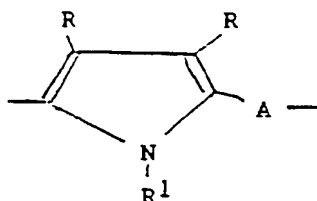
(54) Polymers and processes for their preparation.

(57) A nitrogen-containing polymer is prepared by reacting ammonia or an amine selected from C₁ to C₅₀ primary alkylamines, benzylamine and substituted benzylamines with a linear terpolymer comprised of alternating -CO- and -(A)- units, the -(A)- units comprising a mixture of -CH₂CH₂- units and -CH₂CH(R)- units wherein R is C₁ to C₆ alkyl or phenyl.

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POLYMERS AND PROCESSES FOR THEIR PREPARATION

The present invention relates to new polymeric materials which are comprised, at least in part of units having the general formula



where A, R and R¹ are as defined herein. The present invention also relates to processes for the preparation of such new polymeric materials.

GB 1492172 discloses polymeric materials comprised in part of units of the above formula where both R groups are hydrogen, and -X-is -CH₂CH₂-. Such polymeric materials are made by treating ethylene/carbon monoxide copolymers with a strong acid e.g. concentrated sulphuric acid or trifluoroacetic acid.

US 397374 discloses polymeric pyrrolic derivatives which are prepared by reacting an ethylene/carbon monoxide copolymer with a primary monoamine e.g. methylamine, ethylamine and the like in a solvent e.g. m-creso or hexafluorisopropanol. The materials disclosed have between 4 and 50% of their carbonyl groups converted into pyrrole groups.

J Chem. Soc. Chem. Comm. 1989 p965-966 and Macromolecules 1989 p2012-2014 disclose similar derivatives of ethylene/carbon monoxide copolymers in which up to 88% of the carbonyl groups have been converted to pyrrole groups.

Finally, J Amer. Chem. Soc. (1954) p6394-6399 discloses the reductive amination of ethylene/carbon monoxide copolymers but does not teach the formation of pyrrole groups.

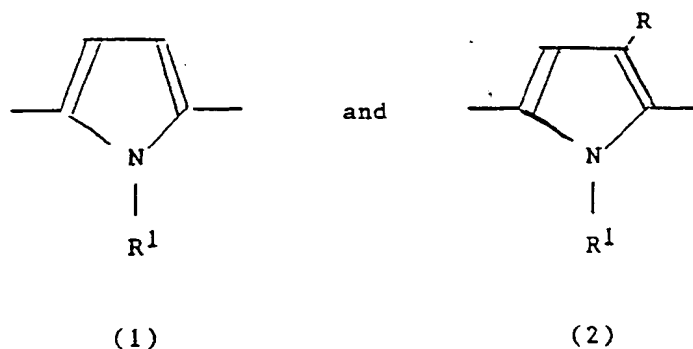
A family of pyrrolic derivatives of ethylene/alpha-olefin/carbon monoxide terpolymers has now been developed which it is believed will find use as a speciality plastic in the chemical industry. Possible uses for such materials include, for example, removal of metals from liquids or as supports for Group VIII noble metal catalysts.

The ethylene/alpha-olefin/carbon monoxide terpolymers used in preparing the pyrrolic derivatives of the present invention have been disclosed in for example EP 213671.

According to the present invention there is provided a nitrogen-containing polymer prepared by reacting ammonia or an amine selected from C₁ to C₅₀ primary alkylamines, benzylamine and substituted benzylamines with a linear terpolymer comprised of alternating -CO- and (A) units, the (A) units comprising a mixture of -CH₂CH₂- units and units of formula -CH₂CH(R)- wherein R is C₁ to C₆ alkyl or phenyl.

Most preferred reactants for preparing the nitrogen-containing polymers of the present inventions are (1) ammonia and C₁ to C₂₀ primary alkylamines and (2) linear terpolymers comprised of alternating CO and (A) units where the (A) units are a mixture of -CH₂CH₂- and -CH₂-CH(CH₃)- or -CH₂-CH(C₂H₅)- units. Typically the molar ratio of the -CH₂CH₂- to -CH₂CH(R) units in the terpolymer should be in the range 5:1 to 200:1 preferably 10:1 to 100:1.

The nitrogen containing polymers of the present invention are comprised of (a) the two pyrrole units



15 where R^1 is selected from hydrogen, C_1 to C_{50} alkyl, phenyl or substituted phenyl, and (b) units of formula $-\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{R})-$. Optionally the polymer may contain unreacted $-\text{CO}-$ units provided that they comprise no more than 50 mole % preferably no more than 20 mole % of the number of $-\text{CO}-$ units present in the original terpolymer. Since the ratio of $-\text{CH}_2\text{CH}_2-$ to $-\text{CH}_2\text{CH}(\text{R})-$ units in the terpolymer is suitably in the range 5:1 to 200:1 it can be expected that in most cases the nitrogen-containing polymer will comprise
20 more pyrrole units of formula (1) than pyrrole units of formula (2).

The polymers of the present invention are suitably prepared by reacting the linear terpolymer and the ammonia or amine at a temperature in the range $15-150^\circ\text{C}$ (preferably $30-100^\circ\text{C}$) optionally in the presence of a solvent. For high temperatures it may be necessary to carry out the reaction in a sealed vessel under an autogenous pressure of the contents. The terpolymer is suitably one prepared by the
25 process disclosed in EP 213671 i.e. terpolymerisation of ethylene, carbon monoxide and an alpha olefin of formula $\text{RCH}=\text{CH}_2$ in the presence of a phosphine modified palladium catalyst. However, it is contemplated that similar palladium catalyst systems carrying out essentially the same reaction could be used.

The invention is now illustrated by the following examples.

30 Example 1 - Preparation of Ethylene/Propylene/CO terpolymer

A 300ml stainless steel autoclave was charged with methanol (100ml) and the palladium complex $[-(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{Pd}(\text{PhCN})_2]\cdot 2\text{BF}_4$ (0.089g). The autoclave was sealed and air was flushed out by
35 pressurising and venting three times with 3 bar of a 44:6:50 mole ratio mixture of ethylene, propylene and CO. After flushing the autoclave was pressurised to 50 bar with the same mixture and heated to 100°C . The autoclave was maintained at this temperature for three hours during which time more of the mixture was added to maintain a pressure of 50 bar. At the end of three hours the autoclave was cooled to room temperature and the excess pressure vented. 20.1g of terpolymer (ethylene/propylene/carbon monoxide)
40 was removed from the autoclave, along with the methanol and catalyst. The terpolymer was separated by filtration washed with methanol and dried.

45 Example 2 - Preparation of Nitrogen-Containing Polymer

2.9g of the terpolymer described above was charged to a 150ml stirred stainless steel autoclave together with 30 mls of 25% aqueous methylamine. The autoclave was sealed and heated to 100°C for
50 eighteen hours during which time the contents were stirred. At the end of this time the autoclave was cooled to room temperature and the contents removed. The contents, a suspension of solid product in the liquid medium, were subjected to filtration to isolate the solid product. The solid product was then washed with 2×25 mls of distilled water and then dried at 100°C to give 2.79g of a pale brown powder containing 11.1% by weight nitrogen. Analysis by NMR indicated the presence of pyrrole units in the product.

55 Example 3 - Preparation of Nitrogen-Containing Polymer ($R^1 = \text{C}_{16}$)

The terpolymer of Example 1 (2.0g) and hexadecylamine (10.21g, 0.042 moles) together with H_2O (30 ml) were heated to 120°C for 17h. The excess amine was then extracted by washing with 2×250 ml

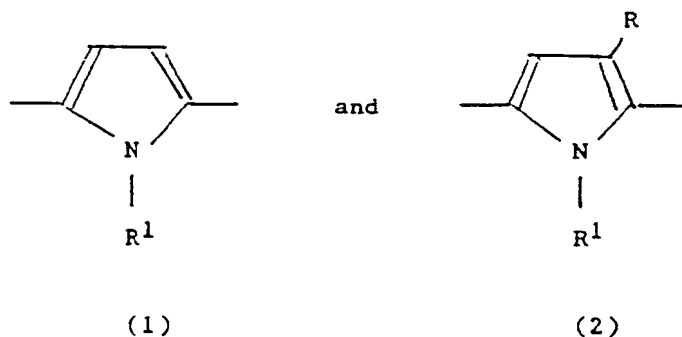
portions of acetone. The product was collected by filtration to give 3.738g of a pale brown powdery solid.
o CHN analysis 80.9 %C 12.3 %H 4.1 %N
o m.p. 50-55 ° C.

Example 4 - Preparation of Nitrogen-Containing Polymer ($R^1 = C_{18}$)

The terpolymer (1.5g) and octadecylamine (6.0g 0.22 moles) in 50 ml of H₂O were heated to 120° C for 16h. The excess amine was extracted with 2 x 250 ml portions of acetone to give a brown solid. The product was collected by filtration and dried (Yield = 4.35g) CHN analysis 81.9% C, 12.5% H, 4.6% W, mp 60-70° C.

Claims

1. A nitrogen-containing polymer prepared by reacting ammonia or an amine selected from C₁ to C₅₀ primary alkylamines, benzylamine and substituted benzylamines with a linear terpolymer comprised of alternating -CO- and -(A)- units the -(A)- units comprising a mixture of -CH₂CH₂- units and -CH₂CH(R)- units wherein R is C₁ to C₆ alkyl or phenyl.
2. A nitrogen-containing polymer as claimed in claim 1 wherein the linear terpolymer employed in its manufacture is comprised of alternating -CO- and -(A)- units in which -(A)- is a mixture of -CH₂CH₂- and -CH₂CH(CH₃)- or -CH₂CH(C₂H₅)-.
3. A nitrogen-containing polymer comprised of (a) pyrrole units of formula



wherein R¹ is selected from hydrogen, C₁ to C₅₀ alkyl, phenyl or substituted phenyl and R is C₁ to C₆ alkyl or phenyl and (b) units of formula -CH₂CH₂- and -CH₂CH(R)-.

4. A nitrogen-containing polymer as claimed in claim 3 further comprising -CO- units.

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27.03.91 Bulletin 91/13(71) Applicant: **The British Petroleum Company
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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90305685.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	<u>US - A - 3 979 374</u> (KIOVSKY) * Abstract *	1-4	C 08 G 67/02 C 08 G 73/06
P, A	<u>EP - A2 - 0 324 998</u> (SHELL) * Claims 1-10; example 1 *	1-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 G
The present search report has been drawn up for all claims.			
Place of search VIENNA		Date of completion of the search 17-12-1990	Examiner ONDER
CATEGORY OF CITED DOCUMENTS			
I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons X : member of the same patent family, corresponding document A : particularly relevant if taken alone V : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EP FORM (01/01/91) (P.0001)